SYNTHESIS OF A NEW MODIFICATION OF ALUMINUM OXIDE WITH THE SPINEL STRUCTURE UNDER SHOCK-WAVE ACTION ON GIBBSITE

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A new modification of aluminum oxide γ_1-Al_2O_3 with the spinel structure was produced under shock-wave impact on gibbsite. The parameter of the face-centered lattice $a = 7.935(1)$ Å. The x-ray pattern and the indexing results are presented. The methods of synthesis are described.

The study in [1] presents the results of an x-ray analysis of the products obtained under shock-wave impact on gibbsite $Al_2O_3 \cdot 3H_2O$ in terms of axially symmetric loading [2] in a steel preservation ampoule. The ampoule design made it possible to localize the aftereffects of gibbsite decomposition by explosion and to preserve the sample in which the spinel $FeAl_2O_4$ with the tetragonal distortion of the cubic lattice was identified.

The diffusion coefficient for the conditions implemented in the preserved sample can be taken equal to 4×10^{-3} cm^2/sec [3]. Consequently, the time of iron penetration by diffusion into a gibbsite layer 0.1 cm thick will be 2.5 sec. This is 10^6 times more than the time of existence of high pressure inside the preservation ampoule, i.e., $(4-5) \times 10^{-6}$ sec. Therefore, we have to assume either the presence of intense hydrodynamic mixing of the reaction components in the preservation ampoule, or a significant increase in the diffusion coefficient in the range of high pressure and temperature gradients.

The present paper describes the results of the x-ray analysis of a sample obtained under conditions preventing the interaction of the gibbsite transformation products with the iron wall (Fig. 1) As distinct from the previous experiment, a gibbsite sample weighing 0.04 g with density 1.2 g/cm^3 was placed into the narrow channel *1* (2 mm in diameter) of the thick-walled aluminum vessel *2* (8 mm in diameter) positioned coaxially with respect to the axis of the steel cylindrical preservation ampoule *3* (external diameter 13 mm). The shock-wave loading was implemented by a gliding detonation wave produced by explosion of octogen charge *4* with a bulk density of 1.12 g/cm^3 placed inside the steel shell *5*. The detonation speed was 6150 m/s and the pressure on the detonation wave front was 12.5 GPa.

The detonation was initiated by the explosion of the azide drop *6* though the flat-wave generator *7*. In order to avoid the destruction of the preservation ampoule caused by the fracture phenomena, its lower end was placed in contact with a thick steel slab *8*.

The x-ray phase analysis was carried out with $CuK_{\alpha 1}$ radiation in the focusing monochromator chamber FR-552 (germanium as the reference standard). Measurement of the x-ray patterns was carried out on an IZA-2 comparator. The line intensities were assessed by the blackening marks according to the 100-grade scale. The initial gibbsite (analytical grade, GOST 11841–66) was subjected to x-ray analysis.
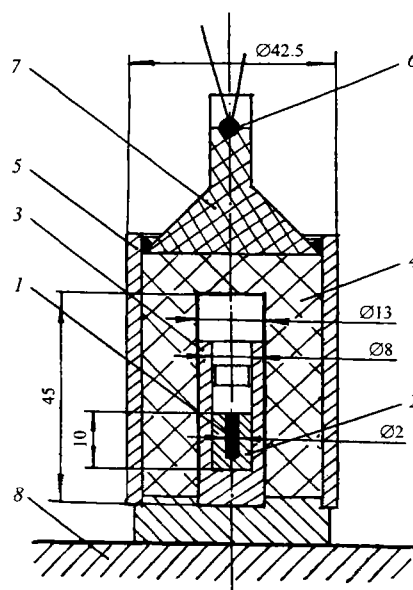

Fig. 1. Design of the explosive charge and the preservation ampoule used in the experiment.

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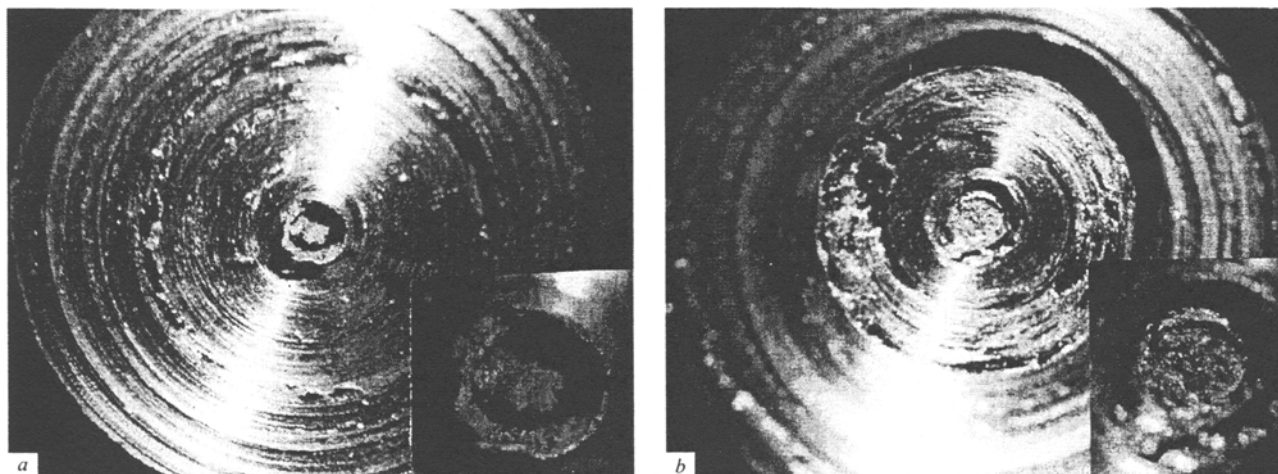
Fig. 2. Cross-lateral section of the preservation ampoule and magnified photo of the central channel after the explosion in the experiments with gibbsite (a) and corundum (b).

The x-ray data correspond to the published data (ASTM-7 – 324).

It should be noted that two modification of high-pressure $Al(OH)_3$ were previously obtained using the high-pressure tempering method. In the study described in [4], a phase of $Al(OH)_3$ II with the primitive cubic lattice, which is metastable in normal conditions, was produced at a steam pressure of ~7 GPa at a temperature of 400°C. The lattice parameters are $a = 7.20$ Å, $z = 8$, and estimated density 2.77 g/cm³. At atmospheric pressure and a temperature of 363°C, $Al(OH)_3$ II changes over to corundum. The second phase δ-$Al(OH)_3$ is formed in the treatment of any modification of $Al(OH)_3$ and also mixtures of boehmite with water within the pressure range of 1.5 – 7.0 GPa and at temperatures above 200°C. When heated up to 430°C, δ-$Al(OH)_3$ is transformed to γ-Al_2O_3. The x-ray pattern of δ-$Al(OH)_3$ corresponds to the primitive rhombic lattice with the parameters (Å): $a = 5.141$, $b = 5.063$, $c = 7.259$, $z = 2$; density 2.802 g/cm³ [5].

After the experiment, the ampoule was opened. It was discovered that the aluminum vessel was preserved but its walls had undergone strong mechanical deformation. There is a through opening along the vessel axis (Fig. 2a). The product of the gibbsite transformation in the form of a gray crystalline compound was partly located on the channel

walls, and also in the form of a compact rod located along the channel axis.

The x-ray analysis results of the gray crystalline compound, which is the product of the transformation of $Al(OH)_3$ under shock-wave impact, are given in Table 1. All seven lines of the x-ray pattern were indexed in the cubic face-centered lattice with parameter $a = 7.935(1)$ Å and the elementary cell volume $V = 499.7(2)$ Å.

The criterion of correct indexing of seven lines of the x-ray pattern $M(7) = 70.7$, which bears out the reliability of the indexing. The line with $hkl = 200$ is absent on the x-ray pattern. The hkl indexes of the patterns give a possibility at this particular stage of the x-ray analysis to select the Fedorov group $Fd3m$ in which the compounds with the spinel structure are crystallized [6] and, in particular, γ-Al_2O_3 which has the defective spinel structure: out of 24 cation vacancies, one-third of the vacancies are occupied by aluminum atoms. Part of the aluminum atoms are arranged in the tetrahedral positions. The cation distribution is expressed by the formula $Al_{0.67}\square_{0.33}[Al]_2O_4$.

The x-ray pattern shown in Table 1 cannot be indexed with the lattice parameter of γ-Al_2O_3. The published data [7] and the data available in the PDF ICPDS x-ray database (74-2206, 77-0396, 77-0403, 79-1557, 79-1558, 80-0955) indicate that the parameter of the nondistorted cubic lattice γ-Al_2O_3 is significantly smaller: 7.906 – 7.914 Å. The estimated density for $a = 7.908$ Å and $z = 8$ is equal to 3.658 g/cm³.

The results of the x-ray study give reason for the assumption that a new aluminum oxide modification with the spinel structure was formed under shock-wave impact on gibbsite. The increase in the lattice parameter can be caused by a significant decrease in the degree of defectiveness in the tetrahedral position ($8a$ in the Fedorov group $Fd3m$). The absence of single-crystal data does not allow for unambiguous solution of this problem.

TABLE 1

Intensity	Interplanar distances D_c, Å	$Q = 10^4/D_c^2$	hkl	$Q = 10^4/D_v^2$	ΔQ
13	4.5814	476.43	111	476.44	−0.01
39	2.8087	1267.62	220	1270.51	−2.89
100	2.3919	1747.89	311	1746.95	0.94
13	2.2929	1902.08	222	1905.76	−3.68
75	1.9837	2541.25	400	2541.02	0.23
40	1.5267	4290.33	333	4287.97	2.36
100	1.4028	5081.69	440	5082.04	−0.35

It is known that as gibbsite dehydrates, whether in thermal treatment or in an explosion [7], topotaxy is observed, i.e., continuity of the structural fragments in the dehydration products in the resulting metastable aluminum oxides.

The data in [5] also lead us to assume that the new oxide aluminum modification with the spinel-type structure obtained by us under shock-wave impact was formed from the high-pressure phase δ-Al(OH)$_3$ according to a topotaxic reaction.

In [8], crystals of another oxide aluminum modification (δ-Al$_2$O$_3$) with the spinel structure were grown from the melt. The cubic lattice parameter of δ-Al$_2$O$_3$ ($a = 7.948(2)$ Å) differs insignificantly from the lattice parameter of the aluminum oxide obtained by us under shock-wave impact on gibbsite. However, the relative line intensities of δ-Al$_2$O$_3$ x-ray pattern significantly differ for the same indexes of hkl. All this suggests that we have obtained a new modification of aluminum oxide with the spinel structure. We designated this modification γ_1-Al$_2$O$_3$.

Study of the δ-Al$_2$O$_3$ crystals described in [8] revealed that the $8a$ position is fully occupied, and the $16d$ (octahedric) position is occupied to the extent of 0.832. Thus, the cation distribution in δ-Al$_2$O$_3$ can be expressed by the structural formula Al[Al$_{5/3}$ $\square_{1/3}$]O$_4$, which significantly differs from γ-Al$_2$O$_3$.

In addition to the described experiment, a supplementary experiment was carried out, in which the reaction mixture was prepared by thoroughly mixing equal quantities of corundum and aluminum powders (average particle size 10 µm). No modification of the structure occurred in the same shock-wave impact conditions. The central channel of the ampoule (Fig. 2b) was completely filled with the compressed mixture. The central channel diameter of the ampoule decreased to 0.7 mm.

It was first demonstrated in [6] that the cations A^{2+} in the formation of spinel Al[B]$_2$O$_4$ occupy the tetrahedral vacancies, and the cations B^{3+} fill the tetrahedral vacancies in the cubic face-centered lattice. There are 31 ions of O^{2-}, 8 cations of A^{2+}, and 16 cations of B^{2+} per one elementary cell. The cation distribution over the structural nonequivalent positions in spinel depends on the cation nature, the temperature, and the synthesis conditions. The formula Al[B]$_2$O$_4$ characterizes the structure of what is known as normal spinel.

Franklinite Zn^{2+}[Fe$_2^{3+}$]O$_4^{2-}$, and herzinite Fe^{2+}[Al$_2^{3+}$] O$_4^{2-}$ are normal spinels. If half of the trivalent metal ions occupy the tetrahedral position A, the spinel is called inverted B[AB]O$_4$.

Some examples of inverted spinels are magnetite Fe^{3+}[Fe^{2+}Fe^{3+}]O$_4^{2-}$ and trevorite Fe^{3+}[Ni^{2+}Fe^{3+}}O$_4^{2-}$. Many spinels are characterized by intermediate degrees of inversion λ: B$_\lambda$A$_{1-\lambda}$[B$_{2-\lambda}$A$_\lambda$]O$_4$. The value of λ depends both on the composition and the temperature.

Magnesioferrite MgFe$_2$O$_4$ is capable of modifying λ within a wide range. At high temperatures, $\lambda = 0.67$, and the cation distribution among the tetrahedral and octahedral positions (vacancies) becomes statistical. In natural conditions the noble spinel MgAl$_2$O$_4$ is close to normal, and when it is grown from melts, it becomes partly inverted. The sizes of tetrahedral voids in the densest packing are smaller that those of octahedral voids. Therefore, the tetrahedral vacancy is taken by the ion with the smaller radius. The radius of the trivalent cation is usually smaller than that of the bivalent, which contributes to the formation of the inverted spinel structure. The effective radii of certain metals forming spinels are as follows (Å): Al^{3+} — 0.57, Fe^{3+} — 0.67, Fe^{2+} — 0.83, Mg^{2+} — 0.78, Zn^{2+} — 0.82, Ni^{2+} — 0.78.

It can be assumed that the decrease in the symmetry of the spinel synthesized by us [1] is related to the formation of inverted spinel with the intermediate degree of inversion λ. As the result, a superstructure emerged which caused the tetragonal distortion of the lattice of the compound.

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